A New, Simple Synthesis of 5′-Substituted 1,1′:3′,1″-Terphenyls

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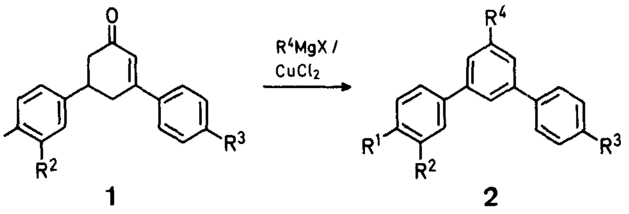
We have found that 1,5-diaryl-3-oxocyclohexenes **1** only reluctantly undergo 1,4-addition of Grignard reagents in the presence of copper(I) chloride whereas facile 1,2-addition across the carbonyl function occurs in the presence of copper(I) chloride or anhydrous copper(II) chloride. In fact, in the presence of copper(II) chloride, reaction of **1** with Grignard reagents proceeds via 1,2-addition, dehydration, and dehydrogenation to give the 5′-substituted 1,1′:3′,1″-terphenyls **2** (or, when $R^4 = C_6H_5$: 1,1′:3′,1″:5′,1‴-quaterphenyls) in yields of 70% or higher in a single-stage synthesis (Table).



2	R^1	R^2	R^3	Substrate **1**	R^4
a	H	H	H	**1a**	C_6H_5
b	H	H	H		CH_3
c	H_3CO	H	H	**1c**	CH_3
d	H_3CO	H	H		C_6H_5
e	H_3C	H	H	**1e**	C_6H_5
f	H_3C	H	CH_3	**1f**	C_6H_5
g	H_3CO	H	CH_3	**1g**	C_6H_5
h	—O—CH_2—O—		H	**1h**	C_6H_5

Reaction of **1a** with phenylmagnesium bromide in the presence of copper(I) chloride proceeds through 1,2-addition at the carbonyl function and dehydration to give 1,3,5-triphenylcyclohexa-1,3-diene. On refluxing a solution of this product in benzene in the presence of copper(II) chloride, the yellow solution develops a dull-red colour which subsequently disappears. After 3 h product **2a** can be isolated; compounds **2** can thus also be obtained in a two-step process.

1,1′:3′,1″:5′,1‴-Quaterphenyl (**2a**) was previously prepared from 1,3,5-triphenylcyclohexa-1,3-diene by dehydrogenation with 10% palladium on carbon[1] or by bromination and dehydrobromination of the diene[2]. Other methods of preparation of the title compounds start from phenylacetylenes[3], acetophenones[4], 4′-methyl-2,4,6-triphenylbenzophenones[5], or 4,6-dimethyl-α-pyrones[6].

In addition to its elegance and simplicity, our method has the advantage of placing substituents in the required position of any or all of the phenyl rings and gives superior yields than the previously reported procedures.

1,5-Diaryl-3-oxocyclohexenes 1:
1,5-Diphenyl-3-oxocyclohexene[7] (**1a**), 5-*p*-anisyl-1-phenyl-3-oxocyclohexene[8] (**1c**), and 5-*p*-anisyl-1-*p*-tolyl-3-oxocyclohexene[8] (**1g**) were prepared as described in the literature. 1-Phenyl-5-*p*-tolyl-3-oxocyclohexene (**1e**; yield: ~68%; m.p. 95–97 °C), 1,5-bis[*p*-tolyl]-3-oxocyclohexene (**1f**; yield: 68%; m.p. 96–98 °C), and 1-phenyl-5-(3,6-methylenedioxyphenyl)-3-oxocyclohexene (**1h**; yield: 68%; m.p. 119–120 °C) were prepared according to the method of Ref.[8] and recrystallised from aqueous ethanol.

Table. 1,1′:3′,1″-Terphenyls and 1,1′:3′,1″:5′,1‴-Quaterphenyls **2a-h**

Product	Yield [%]	m.p. [°C]	Molecular formula[a] or Lit. m.p. [°C]	^{1}H-N.M.R. ($CDCl_3$/TMS)[b] δ [ppm]
2a	73	167–168°	171–172° [1]	7.6 (m, 18 H_{arom})
2b	77	131–132°	130° [6]	2.50 (s, 3 H, OCH_3); 7.5 (m, 13 H_{arom})
2c	79	102–103°	$C_{20}H_{18}O$ (274.3)	2.58 (s, 3 H, CH_3); 3.85 (s, 3 H, OCH_3); 7.5 (m, 12 H_{arom})
2d	79	135–136°	138° [9]	3.80 (s, 3 H, OCH_3); 7.5 (m, 17 H_{arom})
2e	77	124–125°	123.5–124.5° [10]	2.40 (s, 3 H, CH_3); 7.5 (m, 17 H_{arom})
2f	79	135–137°	$C_{26}H_{22}$ (334.4)	2.40 (s, 6 H, CH_3); 7.4 (m, 16 H_{arom})[c]
2g	77	110–112°	$C_{26}H_{22}O$ (350.4)	2.35 (s, 3 H, CH_3); 3.75 (s, 3 H, OCH_3); 7.4 (m, 16 H_{arom})[c]
2h	70	95–96°	$C_{25}H_{18}O_2$ (350.4)	5.90 (s, 2 H, OCH_2O); 7.3 (m, 16 H_{arom})[c]

[a] Satisfactory microanalyses obtained for all new compounds (C ± 0.10, H ± 0.08).

[b] Perkin-Elmer R-32 spectrometer operating at 90 MHz.

[c] In CCl_4 solution.

5′-Substituted 1,1′:3′,1″-Terphenyls 2; Typical Procedure:
A solution of phenylmagnesium bromide prepared from magnesium turnings (0.3 g) and bromobenzene (2 ml) in dry ether (30 ml) is rapidly filtered through glasswool in an atmosphere of nitrogen to remove excess magnesium and other solid particles. To this solution is added with stirring anhydrous copper(II) chloride (0.5 g) in small portions. After stirring for 30 min at room temperature, a solution of **1a** (1 g) in dry benzene (20 ml) is added over a period of 10 min. The mixture is stirred and heated under reflux on a water bath for 3 h and the contents left overnight. The Grignard complex is carefully decomposed with water (~2 ml). The organic layer is decanted, washed with water (10 ml), dried with magnesium sulphate, and the solvent evaporated. The product *1,1′:3′,1″:5′,1‴-quaterphenyl* (**2a**) is crystallised from 1:1 benzene/alcohol; yield: 0.9 g (73%); m.p. 167–168 °C (Ref.[1], m.p. 171–172 °C).

1,3,5-Triphenylcyclohexa-1,3-diene:
The Grignard reagent is prepared from magnesium turnings (3 g) and bromobenzene (18 g) in dry ether (100 ml). Copper(I) chloride (1.1 g) is added to the stirred solution keeping the temperature at 0 °C. The mixture is stirred for 15 min, and to this is then added **1a** (10 g) in dry benzene (60 ml) at 0 °C during 30 min. After stirring for 3 h at 0 °C the mixture is carefully hydrolysed with water (20 ml). The organic layer is separated, washed with water (50 ml), and dried with magnesium sulphate. After removal of the solvent, 1,3,5-triphenylcyclohexa-1,3-diene is obtained; yield: 9.1 g (73%); m.p. 109–110 °C (from ethanol) (Ref.[1], m.p. 108.5–109.5 °C).

^{1}H-N.M.R. (CCl_4): $\delta = 2.8$ (m, 2 $H_{methylene}$); 3.85 (m, 1 $H_{benzylic}$); 6.6 (d, 1 $H_{olefinic}$); 6.65 (s, 1 $H_{olefinic}$); 7.25 ppm (m, 15 H_{arom}).

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